91602
new 82-10

ontario hydro
research division

COMPLIMENTARY COPY
Please Credit Ontario Hydro Research if
Reproduced in Whole or in Part

To: DR. D. MILLS
Director of Research

NO_x Emissions From Soils

M. MacKay
Student
Environmental Science Section
Chemical Research Department

ABSTRACT

The role of NO_x ($NO + NO_2$) in atmospheric chemistry is briefly discussed. The total global source term for NO_x is estimated at 45×10^{12} g N a^{-1}, biogenic production from soils accounting for approximately 15% of this while anthropogenic sources contribute about 63%. Soil flux measurements over a range of environmental conditions are reviewed and factors affecting the emission of NO_x from soils are examined. NO_x fluxes were found to vary over 4 orders of magnitude (0.01 to 390 ng N m^{-2} s^{-1}) and were sensitive to changes in environmental conditions, notably soil temperature and soil moisture. Maximum fluxes occurred for higher soil temperatures (below 50°C) and nitrate contents, and for moderate soil moisture levels.

job	file	date	report no.
35-582-091	837.261	September 6, 1988	88-209-K

LEGAL NOTICE

This report was prepared by Ontario Hydro and, while effort has been made to assure the accuracy and applicability of the material contained herein, neither Ontario Hydro nor any person acting on its behalf:

(a) makes any warranty, express or implied with respect to the use of any information, apparatus, method or process disclosed in this report or that such use may not infringe privately owned rights; or

(b) assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process disclosed in this report.

1.0 INTRODUCTION

NO_x is considered a critical component of global atmospheric chemistry as it is involved in the mechanisms that regulate the production of ozone and the OH radical, the most important oxidants in the troposphere; and the production of HNO_3, which presently contributes about 30 to 50% of the acidity in precipitation (Mooney et al, 1987). There are several known sources of tropospheric NO_x, but the contribution of each to the global NO_x budget is not accurately known (Table 1). Average values from the 5 papers presented in Table 1 are summarized below:

fossil fuel combustion	38%
biomass burning	25%
biogenic production	15%
lightning	13%
NH_3 oxidation	6%
from stratosphere	2%
aircraft	0.6%
Total	45×10^{12} g N a^{-1}

At the regional level the relative proportions of these sources can be altered considerably. Logan (1983) suggests that in North America the combustion of fossil fuels produces 3 to 13 times as much NO_x as natural sources; and in urban centres it is thought that 75% of NO_x is due to automotive exhaust (Lenner, 1987).

The most uncertain NO_x source term is thought to be biogenic production (Table 2), and this is due in part to the great variability in reported flux values, and to the relatively few number of studies undertaken to accurately measure soil emissions. Soil fluxes range over 4 orders of magnitude: 0.01 to 390 ng N m^{-2} s^{-1}, (Slemr and Seiler, 1984; Table 3): and appear to be sensitive to continually changing chemical and physical parameters such as:

- air and soil temperature
- soil moisture content
- soil nitrogen content
- soil O_2 content
- soil bulk density
- ground level ambient NO_x concentration, and surface vegetation effects

(Anderson and Levine, 1987; Johansson, 1984; Johansson and Granat, 1984; Lipschultz et al, 1981; Nishimura et al, 1986; Slemr and Seiler, 1984; Williams et al, 1987; Kimball and Lemon, 1971; Denmead, 1979).

TABLE 1

GLOBAL TROPOSPHERIC SOURCES OF NO

(Tg N a^{-1})

	Bulch et al 1982	Ehhalt & Drummond, 1982	Logan 1983	Stedman & Shetter 1983	National Academy of Sciences 1984
Surface Sources					
Fossil fuel burning	8.2-18.5	13.5(8.2-18.5)	21(14-28)	20(18-22)	15-25
Biomass burning	10-40	11.2(5.6-16.4)	12(4-24)	5(1.7-15)	1-10
Biogenic production	0-15	5.5(1-10)	8(4-16)	10(5-20)	1-10
Atmospheric Sources					
Lightning	3-4	5(2-8)	8(2-20)	3-(1.5-6)	2-20
NH_3 oxidation	-	3.1(1.2-4.9)	1-10	1(0.5-2)	$\leq$5
From stratosphere	0.5-1.5	0.6(0.3-0.9)	0.5	1(0.5-2)	0.5-1.5
Aircraft	0.25	0.3(0.2-0.4)	-	-	0.15-0.3
Total	22-80	39(19-59)	50(25-99)	40(27.2-67)	20-70

(From Anderson & Levine, 1987)

TABLE 2

GLOBAL SOIL NO_x EMISSIONS

NO Emissions ($Tg\ N\ a^{-1}$)	Reference	Comments
10	Galbally & Roy, 1978	No correction for diurnal or seasonal variation
14	Lipschultz, 1981	Reported by Anderson & Levine (1987). Used pure cultures of nitrifying bacteria
<11 (NO_x)	Slemr & Seiler, 1984	
10	Levine, 1987	Reported by Williams et al 1987
1-15	Crutzen, 1983	Reported by Slemr & Seiler, 1984
1-10	Ehhalt & Drummond, 1982	Reported by Slemr & Seiler, 1984
0.2-3	Johansson, 1984	

TABLE 3

EMISSIONS FROM SOILS

NO Emissions ($ng\ N\ m^{-2}\ s^{-1}$)	Field Type	Time of Year	Location	Reference
fert. 6.6 unfert. 1.7 (yr ave)	agric. field	ave.for yr	Jamestown, VA Bennett, CO	Anderson & Levine, 1987
grazed 3.5×10^{-2} ungrazed 1.6×10^{-2}	pasture	spring, autumn	Australia	Galbally & Roy 1978
fert. 60 unfert. 0.13-0.8	forest (conif.)	June, Aug-Sept	Sweden	Johansson 1984
fert. 0.95 (NO_x) unfert. 0.2 (NO_x)	flooded rice fields	Dec 10 days	Griffith, New South Wales	Galbally 1987
fert. 0.1-62 unfert. up to 17	agric. field	Apr, July	Kjettslinge, Sweden	Johansson & Granat, 1984
0.08-21	unfert, uncult, ungrazed pasture	Aug-Oct at night	Colorado	Parish et al 1987
0.03-65 ave. 3.0	" "	Aug-Nov	Colorado	Williams et al 1987
(NO_2) 2.8 (NO) 2.2	bare, unfert.		Finthen, GRG Utrera, SPA	Slemr & Seiler 1984
4.9			Windsor	York U.

TABLE 4

COMPARISON OF NO_2 AND NO FLUXES

	Williams 1987	Galbally & Roy 1978	Slemr & Seiler 1984	Johansson & Granat, 1984
NO_2 Flux as % of NO	9.7	<4	125*	5.9

* - on bare soils
- when veg present, the authors found greatly reduced [NO_2]

2.0 THE ROLE OF NO_x IN THE ATMOSPHERE

NO_x plays a critical regulatory role in the formation of photochemical oxidants such as OH, O_3, and PAN (peroxyacetyl nitrate). The hydroxyl radical (OH), is an important atmospheric scavenger, removing a variety of species including CO, CH_4, SO_2, H_2S, and some halogenated hydrocarbons (Logan et al, 1981). The chemistry of OH is complex and the development of mathematical models has been hindered by the lack of information on the distribution of gases such as NO and NO_2. The rates for reactions involving OH vary considerably and are dependent on the concentrations of species such as NO, CO, O_3, and H_2O (Logan et al, 1981; Logan, 1983). The effect of the NO mixing ratio on OH concentration according to a model developed by Logan et al, (1981) is depicted in Figure 1.

Ozone and PAN are considered to be the most adverse of the photochemical oxidants as they are the major irritants in smog and are thought to be the primary cause of the new type of forest injury found in central Europe (Guderian, 1985). It has been demonstrated that ground-level ozone reduces the productivity and yield in natural and agricultural ecosystems (Mooney et al, 1987).

Ozone and PAN are produced through complex interactions involving NO_x, hydrocarbons and sunlight and are thus called secondary pollutants. Ozone formation results from:

$$OH + CO = H + CO_2$$
$$H + O_2 + M = HO_2 + M$$
$$NO + HO_2 = OH + NO_2$$
$$NO_2 + h\nu\ (\lesssim 410\ nm) = NO + O(^3D)$$
$$O(^1D) + O_2 = O_3$$

overall
$$CO + 2O_2 + h\nu = CO_2 + O_3$$

Competing with O_3 formation is this series of reactions:

$$OH + CO = H + CO_2$$
$$H + O_2 + M = HO_2 + M$$
$$HO_2 + O_3 = OH + 2O_2$$

overall
$$CO + O_3 = CO_2 + O_2$$

Net O_3 destruction will occur when the ratio of NO to O_3 is less than 2×10^{-4}. The point at which O_3 production balances destruction is attained when the NO mixing ratio is approximately 4 to 10 pptv at ground level, thus even in the presence of very low amounts of NO_x, net O_3 formation can occur (Crutzen, 1983). As can be seen from the reactions above, NO_x and the odd hydrogen radicals (H, HO_2, OH) are conserved.

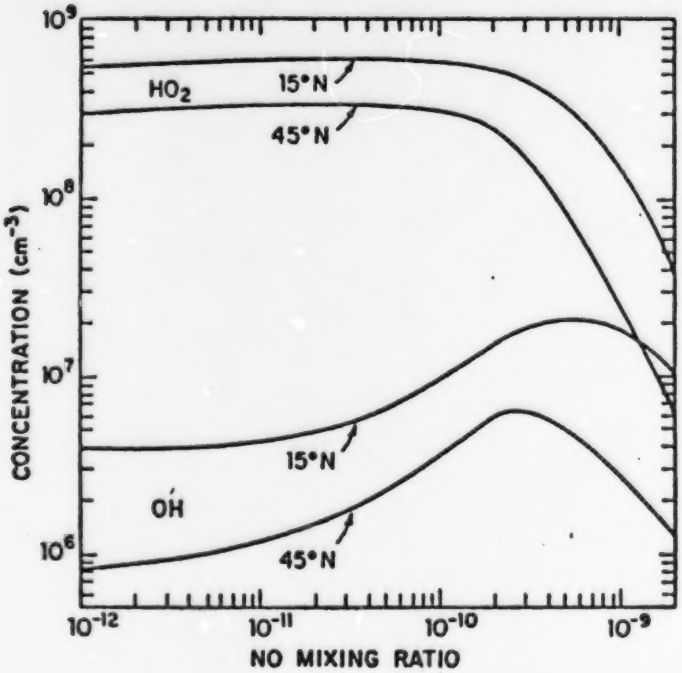

FIGURE 1

VARIATIONS OF HO_2 AND OH WITH NO

Concentrations of OH and HO_2 as a function of the NO mixing ratio. Noon values at the surface are shown for equinoctial conditions at 15°N and 45°N. From Logan et al (1981)

Given sufficient NO_x, increased hydrocarbon emissions can result in enhanced O_3 production since nearly all volatile HC's will react with OH to form peroxy radicals (RO_2) that can oxidize NO to NO_2. NO_x appears to be the limiting element in O_3 formation. It is estimated that only 10% of potential O_3 is presently formed, due to the unavailibility of NO_x (Crutzen, 1983).

The stratosphere may play an important role as a source of tropospheric O_3. The transport of O_3 and NO can occur via tropopausal foldings (exchange time is about 1 month), and slow steady exchange of air (1 to 2 years) (Guderian, 1985).

Tropospheric O_3 is destroyed through its reactions with HC's, NO_x, odd hydrogen and other species; and via photodecomposition and dry deposition. The dry deposition of O_3 to vegetation and soils may oxidize NO before it can escape the ground layer, altering the NO/NO_2 ratio (Delany et al, 1986), and potentially biasing NO/NO_2 flux measurements from soil.

Inhibition of plant growth due to O_3 can be modified by the presence of NO_2. A study found that pretreatment with 0.08 to 0.10 ppm NO_2 for 3 hours followed by exposure to similar levels of O_3 for 6 hours resulted in enhanced reduction of dry weight accumulation (compared to O_3 treatment alone) in radish and wheat plants, but diminished the reduction in bean plants. This effect may be significant during photochemical smog episodes because in daylight, the final O_3 peak is preceded by a peak in NO_2 (Runeckles and Palmer, 1987).

Peroxyacyl nitrates, the most important of which is PAN, are formed by the oxidation of HC's in the presence of NO_x. PAN is a better indicator of photochemical pollution than is O_3 since the latter has a significant natural source (Tsalkani et al, 1987). Appreciable production of PAN {$CH_3C(=O)O_2NO_2$} is not restricted to urban environments but can occur anywhere in the atmosphere. The decomposition of PAN is temperature dependent and thus its atmospheric lifetime increases rapidly with altitude. At ground level its average lifetime is 3 days, at 4 km it is 1 month, and at 8 km, 15 years. In comparison, the average atmospheric lifetime of NO_x is 1.5 days. PAN is not removed by precipitation and is only slowly lost through deposition, thus it is an effective vehicle for long distance transport of NO_x. In polluted air, PAN can reach a concentration of 10 to 20% that of NO_x, and as well as being an eye irritant it is considered to be a major phytotoxicant (Crutzen, 1983).

In the daytime boundary layer O_3, NO and NO_2 rapidly establish an equilibrium (2 to 5 min) via :

$$O_3 + NO = NO_2 + O_2$$
$$NO_2 + h\nu = NO + O(^3D)$$
$$O(^3D) + O_2 + M = O_3 + M$$

and other reactions in which OH and HO_2 play the major radical role (Figure 2). The important atmospheric NO_x reservoirs during the day are HNO_3, PAN and HO_2NO_2. The main NO_x removal mechanism during the day is :

$$NO_2 + OH = HNO_3$$

This reaction is also the major loss mechanism for OH when NO_x levels are high. HNO_3 is removed from the atmosphere relatively quickly (average lifetime, 2 to 6 days) via washout, rainout, aerosol formation (NO_3^-) and dry deposition (Levine et al, 1984).

At night in the absence of photolytic reactions, OH is greatly reduced and a new series of reactions dominate:

$$NO + O_3 = NO_2 + O_2$$
$$NO_2 + O_3 = NO_3 + O_2$$
$$NO_2 + NO_3 = N_2O_5$$
$$N_2O_5 = NO_2 + NO_3$$

(Ehhalt and Drummond, 1982).

These reactions result in a depletion of O_3 and the establishment of an equilibrium involving NO_2, NO_3 and N_2O_5 (Figure 3). NO can be reduced to below detection if there is no local source. N_2O_5 reacts quickly with liquid H_2O (but not vapour) to form HNO_3 which is readily removed from the atmosphere; thus the presence of night-time clouds and fogs efficiently remove NO_x from the air (Ehhalt and Drummond, 1982; Logan, 1983). Both N_2O_5 and NO_3 are rapidly photolyzed in the ensuing dawn (Logan et al, 1981).

Additional night-time HNO_3 formation occurs via the reaction of NO_3 and organics:

$$NO_3 + RCHO = RCO_3 + HNO_3$$
$$NO_3 + HCHO = HNO_3 + HO_2 + CO$$
(equations are unbalanced)

According to one model (Russell et al, 1985) the production of HNO_3 over a 24-h period in an urban environment experiencing photochemical smog is divided as follows:

$NO_2 + OH = HNO_3$	44%	(day)
$N_2O_5 + H_2O = HNO_3$	24%	(night)
NO_3 + organics $= HNO_3$	32%	(night)

This model predicts that, of the NO_x initially present in a polluted urban air parcel, 58% is lost through dry deposition within a 24-h period. This dry deposition is accomplished mainly by HNO_3 (39%), PAN (33%) and NO_2 (24%). At the end of the 24-h period, the major atmospheric end products of the initial NO_x are HNO_3 and PAN.

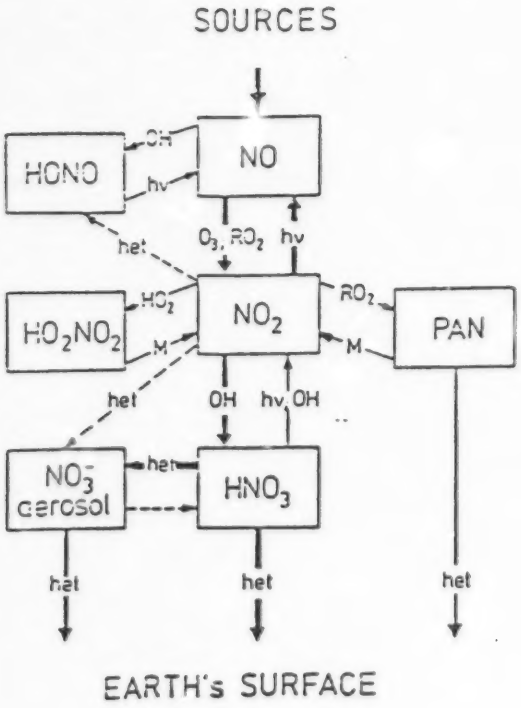

FIGURE 2

DAYTIME REACTION PATHS

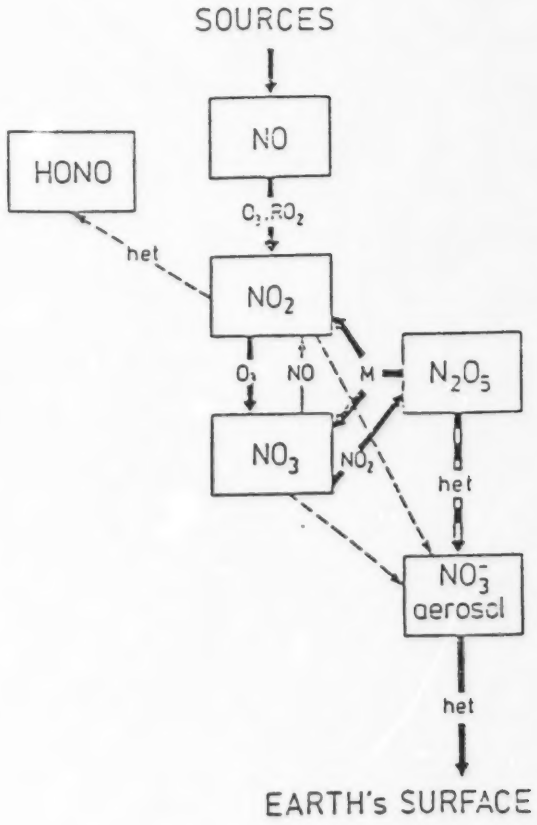

FIGURE 3

NIGHTTIME REACTION PATHS

Major reaction paths for nitrogen oxides in the lower troposphere. The symbols in the boxes denote the major oxidized nitrogen compounds present. They are interconverted by reactions, characterized by the symbols within the arrows. The heavy arrows indicate the main paths and the broken arrows show paths that are thought to be likely but are not well established. "M" represents unimolecular decay; "het" refers to heterogeneous processes, for

(From Ehhalt and Drummond, 1982)

The tropospheric NO_x profile in northern mid-latitudes (30-60° N) is dominated at all altitudes by anthropogenic sources, thus it is unlikely that natural NO_x contributes substantially to the oxidant and acid rain problems. In these latitudes it has been suggested that anthropogenic sources are about 1 order of magnitude greater than natural emissions (Guderian, 1985).

Reported ambient NO_x levels in the clean troposphere range from 0.1 to 5 ppbv over land (Anderson and Levine, 1987; Guderian, 1985) and on the order of 0.01 ppbv over the remote Pacific (Guderian, 1985; Logan, 1983). In U.S. cities the average NO_2 concentration has been found to be 35 ppbv, and in some densely populated areas, levels exceeding 150 ppbv have been reported (Logan, 1983). High oxidant levels are linked to NO_x concentrations of greater than 10 ppbv (Guderian, 1985).

The continuing global increase in biomass and fossil fuel combustion has resulted in ever increasing levels of NO_x, CO and hydrocarbons in the troposphere. Anthropogenic activities are the sources of about one half of the annual CO production (Mooney et al, 1987), 10 to 50% of the annual hydrocarbon production (Guderian, 1985), and 50 to 75% of the annual NO_x production (Anderson and Levine, 1987).

HNO_3, the main storage form of NO_x, is considered to be the fastest growing component of acid precipitation (Anderson and Levine, 1987), presently accounting for 30 to 50% of the acidity (Ehhalt and Drummond, 1982). Surface O_3 levels have been rising at an annual rate of about 1 to 3% over North America and Europe since the late 60's (Dickinson and Cicerone, 1986). It is thought that these increases are largely the result of increased anthropogenic NO_x and hydrocarbon emissions into the troposphere.

3.0 SOIL EMISSIONS OF NO_x

The biogenic production of NO_x (mostly from microbial activity in soils) is considered to be the most uncertain source term (Slemr and Seiler, 1984), due to the demonstrated high sensitivity of the NO_x-forming reactions to various physical and chemical parameters, and due to the fact that a limited number of measurements (encompassing a limited number of environments) have been made. Measured NO_x fluxes from soils cover more than 4 orders of magnitude (Table 3) and appear to be greatly affected by factors including soil temperature, soil moisture and nitrogen content, and ambient NO_x levels (Anderson and Levine, 1987; Galbally and Roy, 1978; Galbally et al, 1987; Johansson, 1984; Johansson and Granat, 1984; Parish et al, 1987; Slemr and Seiler, 1984; Williams et al, 1987). The great variability in reported values may also be due to differences in sampling technique. A number of studies have incorporated closed chambers (Williams et al, 1987; Johansson and Granat, 1984; Anderson and Levine, 1987); open chambers (Johansson and Granat, 1984); the gradient method

(Parish et al, 1987); and eddy correlations (Delaney et al, 1986). These methods may have perturbed the environment to different degrees.

NO has been found to be the dominant NO_x emission species accounting for between 90 and 100% in most studies (Galbally and Roy, 1978; Johansson and Granat, 1984; Slemr and Seiler, 1984; Williams et al, 1987).

It is an intermediate of nitrification in aerobic soils, denitrification in anaerobic soils and is a product of the chemical decomposition of HNO_2 (Johansson and Granat, 1984; Slemr and Seiler, 1984; Williams et al, 1987). The atmospheric lifespan of NO is on the order of seconds to minutes as it is readily oxidized to NO_2.

As shown in Table 4, NO_2 fluxes typically account for 0 to 10% of the total NO_x released from soils, and several studies have failed to detect it at all (Williams et al, 1987). This may be due to the strong affinity of NO_2 for soil particles, its reactivity with humic acids, and that its absorption by soil water is much higher than that of NO (Slemr and Seiler, 1984). The solubility of NO in H_2O is only 4.6 mL per 100 mL at 1 atm and 20°C but NO_2 rapidly decomposes via:

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$
$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O \text{ (especially when warm)}$$

(Cotton and Wilkinson, 1980).

Thus soil H_2O may be responsible for converting a significant amount of NO_2 into NO, which can then pass to the atmosphere as a gas.

NO is not strongly absorbed by soil particles, is not very soluble in water and can pass through the soil to the atmosphere unoxidized at relatively high concentrations (oxidation half-life at 10 ppbv is 10^4 h, at 100 ppm is <1 h) (Galbally and Roy, 1978). Soil absorption of NO_2 increases 10-fold as relative humidity increases from 5% to 95% and in most acid soils, NO_2 is efficiently oxidized to NO_3 (Prather et al, 1973). Vegetation (rush, lawn grass, Ginkgo leaves) has been found to reduce ambient NO_2 to NO, with steady state conversions of up to 70%. This reduction is highly dependent on relative humidity and appears to be mediated by a polysaccharide (Nishimura et al, 1986). Another study has found damp soil and vegetation to strongly absorb ambient NO_2 (Williams et al, 1987).

NO_2 can be produced through the chemical decomposition of HNO_2 (which is an intermediate of nitrification and denitrification) and via microbial pathways (Delany et al, 1986; Ehhalt and Drummond, 1982; Slemr and Seiler, 1984), although the latter is not well understood due to difficulties in measuring NO_2 within the soil system (Slemr and Seiler, 1984).

The wide range of NO_x flux values reported, even over apparently similar surfaces may reflect the sensitivity of the microbial mass to subtle changes in its environment. Temperature appears to have a major effect on NO_x fluxes. Several authors have reported that as soil temperature increased, NO and NO_2 emissions generally increased over several soil types and a variety of environmental conditions, (Anderson and Levine, 1987; Delany et al, 1986; Johansson, 1984; Johansson and Granat, 1984; Slemr and Seiler, 1984; Williams et al, 1987). However, one study found no temperature dependence from 0-25°C over grazed pasture (Galbally personal communication in Johansson and Granat, 1984). Slemr and Seiler (1984) found that NO flux was positively correlated with soil temperature (at 1 cm) but NO_2 flux was positively correlated with solar radiation, and that the maximum NO_2 flux usually occurred a few hours before the maximum NO flux. They suggested that either different processes are involved in the evolution of NO and NO_2, or that NO_2 is produced higher up in the soil column. Due to the affinity of NO_2 for soil particles and water, it seems plausible that NO_2 cannot escape from as great a depth as NO.

Anderson and Levine (1987) found that peak NO fluxes occurred several hours before peak soil temperatures, and suggested that this might have been due to changing soil moisture conditions on water stressed microbes. Delany et al (1986) found an association between NO_x flux and transpiration, and suggested that NO_2 transport may occur through plant vascular systems. This has important implications for the closed chamber technique which can potentially inhibit transpiration. Johansson and Granat (1984) found that NO_x fluxes in the morning hours were more rapid than predicted based on soil temperatures alone, and they suggested that at this time roots exude organic substances that stimulate organic activity.

Soil moisture appears to have a strong influence on NO_x fluxes although no systematic relationship has been found (Anderson and Levin, 1987; Johansson and Granat, 1984; Slemr and Seiler, 1984; Williams et al, 1987). However, from Anderson and Levine's data which are plotted in Figure 4, it is suggested that higher fluxes are associated with higher soil temperatures and medium water contents. NO emissions dramatically increased after irrigation, but once the soil was saturated, very little NO was detected. Emissions of N_2O increased as soil moisture approached and exceeded field capacity (Anderson and Levine, 1987). NO flux increased 10-fold as soil moisture increased from 1% (by weight) to 15%. A one-day delay between irrigation and maximum NO flux was observed. NO_2 flux increased 40-fold and responded much more rapidly to irrigation, suggesting that it is released from higher

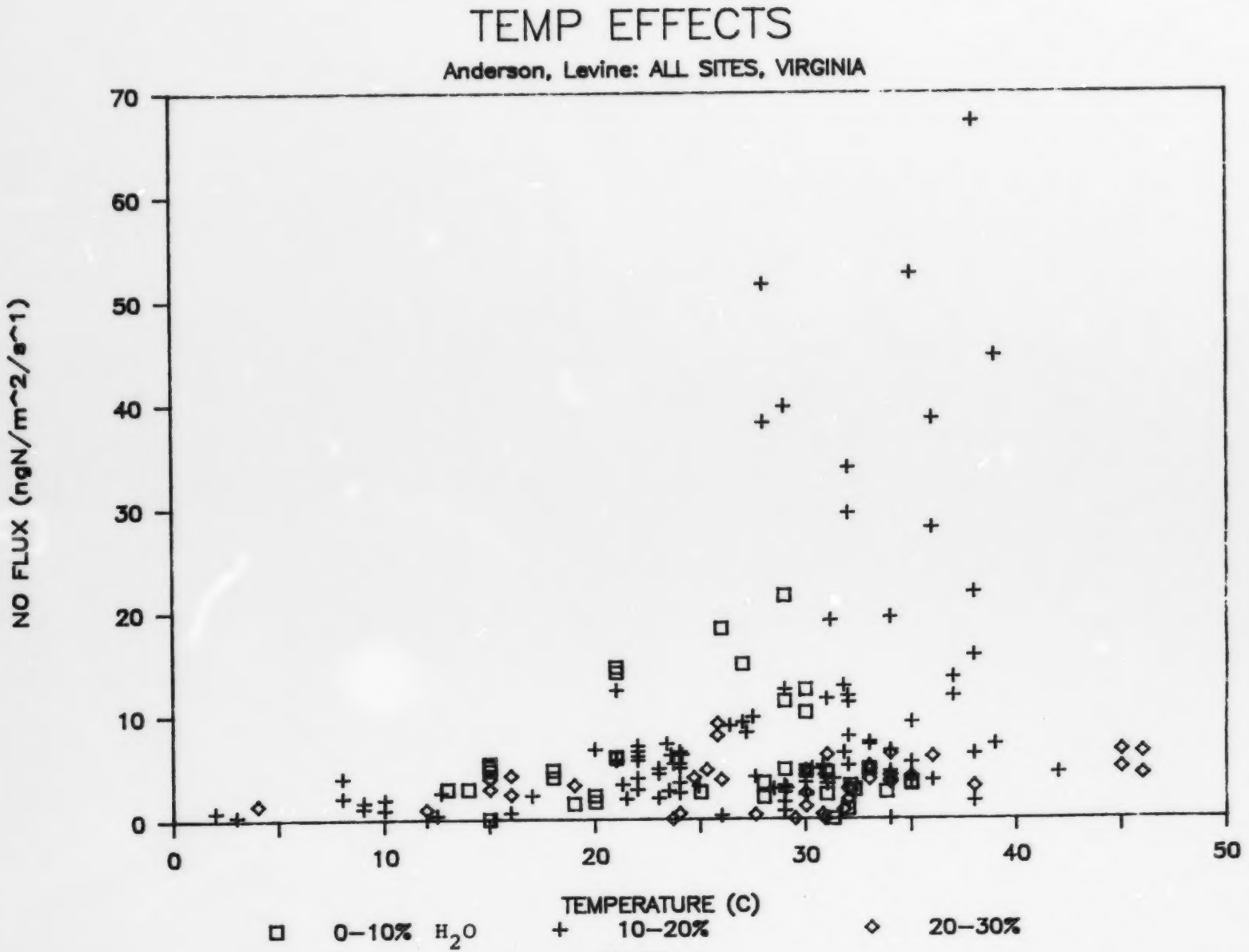
TEMP EFFECTS
Anderson, Levine: ALL SITES, VIRGINIA
NO FLUX (ngN/m^2/s^1)
70
60
50
40
30
20
10
0
0
10
20
30
40
50
TEMPERATURE (C)
0–10% H2O
10–20%
20–30%

FIGURE 4

up in the soil column than NO (Slemr and Seiler, 1984). This effect decreased after successive waterings and disappeared after the fourth irrigation. There is uncertainty regarding whether saturated soil reduces microbial activity, inhibits gaseous escape, or both.

The presence of vegetation appears to reduce NO_x fluxes (even to negative values) but it is difficult to compare vegetated plots to bare plots since many soil parameters are affected by the presence of plants. This flux reduction may be due to:

- a drop in soil temperatures (shading),
- increased organic content in soil,
- increased soil moisture,
- deposition onto plants,
- uptake and metabolism of NO_x by plants, and
- prevention of vertical mixing, resulting in a higher NO_x level near the soil surface, inhibiting diffusion.

The application of fertilizers increases the NO_x flux, and the amount of increase depended on the oxidation state of the fertilizer (Lenner, 1987; Johansson and Granat, 1984; Slemr and Seiler, 1984). The highest fluxes result from the use of ammonium fertilizers, suggesting that an oxidation process like nitrification is the main NO_x source (Slemr and Seiler, 1984). The amount of fertilizer lost as NO_x is generally low, less than 1%. Slemr and Seiler (1984) reported a loss of 5.4% when using urea on bare soil, but found that vegetation greatly reduced this loss. NO fluxes have been correlated with soil nitrate concentrations (Anderson and Levine, 1987).

Changes in air pressure and air turbulence are inherent in the closed box system and may significantly alter the flux of gases between the soil and atmosphere. Denmead (1979) found that a pressure deficit of 1 cm H_2O within his system produced an N_2O flux 10 times that attributed to diffusion alone, and suggested that this was due to mass flow from the soil. Lemon (1978) suggests that under natural conditions mass flow of N_2O due to changes in moisture, temperature, pressure and wind speed are insignificant compared with molecular diffusion processes, but adds that with closed box systems, velocity fluctuations inside have been correlated with air turbulence outside, indicating that mass flow may be a factor.

Pressure changes at the soil surface appear to influence soil gas concentrations several feet down. A study involving soil radon concentrations found substantial barometric pressure and wind speed effects on radon concentrations as much as 5-1/2 ft underground. Radon fluxes from the soil were twice as great on windy days as calm days and were increased by thermally induced vertical air motion (ref cited in Lemon, 1978).

In the nighttime boundary layer, low wind velocities and less air turbulence due to the absence of solar-induced convection can result in reduced vertical mixing and the shielding of surface NO from O_3. This may be the cause of reported morning peaks of ambient NO that were larger than the noon peaks, which are primarily due to NO_2 photodecomposition (Helas et al, 1987).

Air turbulence may play an important role in the exchange of gases between the soil and atmosphere. Using a chamber technique, Johansson and Granat (1984) determined that NO_x emissions in still air were 30-70% of those in stirred air. Air turbulence and vegetation probably affect the concentrations of various gases at the soil-air interface and thus modify diffusion rates in and out of the soil.

NO and NO_2 production is affected by O_2 availability (Johansson and Granat, 1984; Lipschultz et al, 1981). At 0.5% O_2 the molar rates of NO/N_2O as produced by a nitrifying bacteria (under laboratory conditions) was 2.8 to 7.8 and at 20% O_2 was 1.1. Other soil characteristics such as pH and organic matter content are thought to affect microbial activity and thus NO_x emissions (Folorunso and Rolston, 1985). Another consideration is soil type and bulk density, which may affect diffusion rates through the soil.

The effects of these various physical and chemical parameters may have resulted in the wide range of reported NO_x fluxes over time and over space (Table 3). Regarding spatial variation NO_x fluxes varied:

- ±25% over 12 x 4 m (Williams et al, 1987)
- by a factor of 15 over 14 x 8 m (Fertilized) (Johansson and
- by a factor of 35 over 300 m^2 Granat, 1984)

- by a factor of 100 over 10 m^2 (Fertilized)(Slemr and Seiler, 1984)

Spatial variability is greater over fertilized plots than over unfertilized plots and this is probably due to uneven pellet distribution (Johansson and Granat, 1984). For unfertilized plots the major source of variability is probably inhomogeneity of the soil (which decreases as the soil is left undisturbed). Slemr and Seiler (1984) report the presence of individual "hot spots" of up to 50 times the field average, and they attribute this to soil inhomogeneity.

Diurnal and seasonal cycles have been reported (Anderson and Lerner, 1987; Johansson and Granat, 1984; Slemr and Siler, 1984) and these are probably tied in to changes in soil temperature and moisture content. Maximum NO_x fluxes generally occur in early afternoon and minimum fluxes in the early morning. Anderson and Levine (1987) report that winter emissions (Nov to April) ac-

counted for 24% of the annual NO_x released at their Virginia site. They were aware of no other studies indicating winter emissions.

The compensation point for a soil emission gas, ie, the level at which the soil ceases to be a net source and becomes a net sink, varies from 0.2 to 150 ppbv for NO, depending on conditions such as temperature, moisture and emission rate (Johansson, 1984; Johansson and Granat, 1984; Slemr and Seiler, 1984). When the atmospheric level of NO exceeds the local compensation point, net destruction of NO occurs until the compensation point is again reached. The NO and NO_2 compensation points are rarely exceeded in unpolluted environments (Johansson and Granat, 1984; Slemr & Seiler, 1984). Other soil emitted gases exhibiting compensation points are N_2O and CO_2 (Johansson and Granat, 1984).

5.0 CONCLUSIONS

NO_x plays a vital role in controlling the levels of the OH radical, O_3, HNO_3 and other atmospheric constituents, and thus is a key factor in the acid precipitation and photochemical oxidant problems. Emissions from soils are a significant source of NO_x, providing about 15% of global production. Fossil fuel combustion is the strongest NO_x source accounting for about 38% of NO_x production at present.

The contribution of soils to the global NO_x budget is the least well known value, due to the great variability of flux levels and to the relatively few number of studies that have been done. The variability of NO_x fluxes from soils is thought to be due to constantly changing physical and chemical parameters within the soil. Soil temperature, moisture, nitrate, oxygen content, organic carbon, particle density and other factors affect microbial activity and diffusion rates through the soil and ultimately determine NO_x flux to the atmosphere.

Approved by:

O.A. Kupcis
Manager
Chemical Research Department

Prepared by:

M. MacKay
Student
Environmental Science Section

MM/mf

Reviewed by:

for O.T. Melo

O.T. Melo
Supervising Engineer
Environmental Science Section

REFERENCES

Anderson, I.C., and J.S. Levine, 1987. "Simultaneous Field Measurements of Biogenic Emissions of NO and N_2O," J. Geophys. Res. Vol. 92, D1, p 965-976.

Blackmer, A.M., S.G. Robbins, J.M. Bremner, 1982. "Diurnal Variability in Rate of Emission of Nitrous Oxide from Soils," Soil Sci. Soc. Am. J. 46, p 937-942.

Cates, R.L. and D.R. Keeney, 1987. "N_2O Production Throughout the Year from Fertilized and Manured Maize Fields," J. Environ. Qual. Vol. 16, No. 4, p 443-447.

Cicerone, R.J., 1987. "Changes in Stratospheric Ozone," Sci. 237, p 35-42.

Cotton, F.A., G. Wilkinson, 1980. "Advanced Inorganic Chemistry, 4th Ed., John Wiley and Sons, p 426.

Crutzen, P.J., 1983. "Atmospheric Interactions - Homogeneous Gas Reactions of C, N and S Containing Compounds," in The Major Biogeochemical Cycles and Their Interactions, B. Bolin, R.G. Cook (eds), John Wiley and Sons.

Delany, A.C., D.R. Fitzjarrald, D.H. Lenschow, R. Pearson Jr., G.L. Wendel, B. Woodruff, 1986. "Direct Measurements of Nitrogen Oxides and Ozone Fluxes Over Grassland," J. Atm. Chem. 4, p 429-444.

Denmead, O.T., 1979. "Chamber System for Measuring N_2O Emissions from Soils in the Field," Soil Sci. Soc. A.J. 43(1), p 89-95.

Dickinson, R.E., and R.J. Cicerone, 1986. "Future Global Warming from Atmospheric Trace Gases," Nature 319, p 109-115.

Edwards, N.T., 1974. "A Moving Chamber Design for Measuring Soil Respiration Rates," OIKOS 25, p 97-101.

Ehhalt, D., and J.W. Drummond, 1982. "The Tropospheric Cycle of NO_x" in Chemistry of the Unpolluted and Polluted Troposphere, ed, H.W. Georgii and W. Jaeschke, p 219-251, D. Reidel, Hingham, MA.

Folorunso, O.A., and D.E. Rolston, 1984. "Spatial Variability of Field Measured Denitrification Gas Fluxes," Soil Sci. Soc. Am. J. 48, p 1214-1219.

Folorunso, O.A. and D.E. Rolston, 1985. "Spatial and Spectral Relationships Between Field Measured Denitrification Gas Fluxes and Soil Properties," Soil Sci. Soc. Am. J. 49, p 1087-1093.

Galbally, I.E., and C.R. Roy, 1978. "Loss of Fixed N from Soils by NO Exhalation," Nature 275, p 734-735.

Galbally, I.E., J.R. Freney, W.A. Muirhead, J.R. Simpson, A.C.F. Trevitt, P.M. Chalk, 1987. "Emission of NO_x from a Flooded Soil Fertilized with Urea; Relation to Other N Loss Processes," J. Atm. Chem. 5, p 343-365.

Air Pollution by Photochemical Oxidants, 1985, ed. R. Guderian, Springer-Verlag, Berlin, Heidelberg.

Hao, W.M., S.C. Wofsy, M.B. McElroy, J.M. Beer, M.A. Togan, 1987. "Sources of Atmospheric Nitrous Oxide from Combustion," J. Geophys. Res. 92, p 3098-3104.

Helas, G., A. Broll, K. Rumpel, P. Warneck, 1987. "On the Origins of Night-time NO at a Rural Measurement Site," Atmos. Environ. 21(11), p 2285-2295.

Johansson, C., 1984. "Field Measurements of Emissions of NO from Fertilized and Unfertilized Soils in Sweden," J. Atm. Chem 1, p 429-442.

Johansson, C. and L. Granat, 1984. "Emission of NO from Arable Land," Tellus 36B, p 25-37.

Kimball, B.A. and E.R. Lemon, 1971. "Air Turbulence Effects Upon Soil Gas Exchange," Soil Sci. Soc. A. Proc. 35, p 16-21.

Lemon, E., 1978. "N_2O Exchange at the Land Surface," in Nitrogen in the Environment V. 1, ed. D.R. Nielsen, Academic Press, p 493-521.

Lenner, M., 1987. "Nitrogen Dioxide in Exhaust Emissions from Motor Vehicles," Atm. Environ. Vol. 21, No. 1, p 37-43.

Lenschow, D.H., and A.C. Delany, 1987. "An Analytic Formulation for Nitric Oxide and Nitrogen Dioxide Flux Profiles in the Atmospheric Surface Layer," J. Atm. Chem. 5, p 301-309.

Levine, J.S., T. Augustsson, I. Anderson, J. Hoell, Jr., and D. Brewer, 1984. "Tropospheric Sources of NO_x: Lightning and Biology," Atmos. Environ. 18, p 1797.

Lipschultz, F., O.C. Zafiriou, S.C. Wofsy, M.B. McElroy, F.W. Valois, and S.W. Watson, 1981. "Production of NO and N_2O by Soil Nitrifying Bacteria," Nature 294, p 641-643.

Logan, J.A., M.J. Prather, S.C. Wofsy, and M.B. McElroy, 1981. "Tropospheric Chemistry: A Global Perspective," J. Geophys. Res. 86-C8, p 7210-7254.

Mooney, H.A., P.M. Vitousek, and P.A. Matson, 1987. "Exchange of Materials Between Terrestrial Ecosystems and the Atmosphere," Science 238, p 926-932.

Nishimura H., T. Hayamizu, and Y. Yanagisawa, 1986. "Reduction of NO_2 to NO by Rush and Other Plants," Environ. Sci. Technol. 20, p 413-416.

Parish, D.D., E.J. Williams, D.W. Fahey, S.C. Liu, and F.C. Fehsenfeld, 1987. "Measurement of NO Fluxes from Soils: Intercomparison of Enclosure and Gradient Measurement Techniques," J. Geophys. Res. Vol. 92, D2, p 2165-2171.

Prather, R.J., S. Miyamoto and H. Bohn, 1973. "Sorption of Nitrogen Dioxide by Calcereous Soils," Soil Sci. Soc. Am. Proc. 37, p 860-863.

Rosswell, T., 1983. "The Nitrogen Cycle" in The Major Biogeochemical Cycles and Their Interactions, ed. B. Bolin, R.B. Cook, John Wiley and Sons, p 46-50.

Runeckles, V.C. and K. Palmer, 1987. "Pretreatment with NO_2 Modifies Plant Response to Ozone," Atmos. Environ. 21(3), p 717-719.

Russell, A.G., G.L. McRae and G.R. Cass, 1985. "The Dynamics of Nitric Acid Production and the Fate of Nitrogen Oxides," Atmos. Environ. 19, 6, p 893-903.

Seigneur, C., 1987. "Computer Simulation of Air Pollution Chemistry," Environmental Software, Vol. 2, No. 3, p 116-127.

Slemr, F., and W. Seiler, 1984. "Field Measurements of NO and NO_2 Emissions from Fertilized and Unfertilized Soils," J. Atm. Chem. 2, p 1-24.

Stevenson, F.J., 1986. Cycles of Soil: C, N, P, S, Micronutrients, John Wiley and Sons, p 106-215.

Tsalkani, N., P. Perros and G. Toupance, 1987. "High PAN Concentrations During Nonsummer Periods: A Study of 2 Episodes in Creteil (Paris) France," J. Atm. Chem. 5, p 291-299.

Williams, E.J., D.D. Parrish, and F.C. Fehsenfeld, 1987. "Determination of NO_x Emissions from Soils: Results from A Grassland Site in Colorado," J. Geophys. Res. Vol. 92, D2, p 2173-2179.

Zafirious, O.C., and M. McFarland, 1980. "Determination of Trace Levels of NO in Aqueous Solution," Anal. Chem. 52, p 1662-1667.